

Charge carriers of different origin in cuprates as revealed by experiment

Lev P. Gor'kov

*NHMFL, Florida State University, 1800 E P.Dirac Dr., Tallahassee FL 32310, USA and
L.D.Landau Institute for Theoretical Physics of the RAS, Chernogolovka 142432, RUSSIA*

Gregory B. Teitel'baum*

E.K.Zavoiskii Institute for Technical Physics of the RAS, Kazan 420029, RUSSIA

(Dated: February 6, 2008)

The Hall coefficient data for cuprates show that number of carriers exceeds external doping x at higher x and varies with temperature. Hence, spins on the Cu-sites are not conserved. Activation energy for thermally excited carriers equals the energy between the Fermi surface “arc” and the band bottom near the van Hove singularities. Crossover from marginal Fermi liquid- to pseudogap- regime happens at temperatures at which number of activated carriers gets comparable with the number of externally doped holes. Implications for the (T,x) -phase diagram of cuprates are discussed.

The unifying feature for all cuprates is the presence of one or more CuO_2 -planes. The consensus is that the in-plane electronic constituents, namely, the Cu d^9 levels and the oxygen p -orbitals determine all cuprates’ physics [1, 2]. Even this simplified model turns out to be difficult for complete theoretical analysis, and properties of cuprates remain far from being understood. Below, from the experimental stand-point, we address mainly properties of the single-plane cuprates, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO), the materials best studied by now.

Transition from the Mott insulating state into a metallic and superconducting (SC) state is driven in cuprates by external doping. We emphasize from the very beginning that doping, rigorously speaking, is *not* the thermodynamic path for Metal-Insulator (MI) transition.

It is often assumed that initially holes go onto the oxygen sites, since the Cu(d^9)- and the oxygen’s levels in the parent antiferromagnet (AFM) La_2CuO_4 are separated by a “charge transfer gap” of order $\sim 1.2\text{-}1.5$ eV [3]. It becomes less obvious with the increase of concentration, x , because charges of dopant ions result in important changes in the system’s energy balance. Indeed, already at rather small concentrations (as seen from the ARPES data at $x \sim 0.03$ [4]) it is more proper to resort to bands’ description, at least, for the oxygen bands. This gives rise to the hybridization between oxygen and Cu levels, although the Cu(d^9) level tends to partially conserve its local character owing to strong tendency to the Jahn-Teller polaron formation inherent in the d^9 - configuration. Occupied neighboring Cu(d^9)-sites experience strong interactions via mutual local lattice distortions. As to the exchange spin interactions, it is now clear that they play a secondary role by coupling spins on the adjacent sites antiferromagnetically [5, 6].

In what follows we discuss some recent experiments that have shed more light on the problem of the nature and actual number of carriers and on the stability of the Cu d^9 -hole configuration, the latter being responsible for existence of local spin $S = 1/2$ at a given Cu-site.

There are may be some concerns how to formulate such

a question. Indeed, the (T,x) plane for cuprates, e.g., $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, is sub- divided into two main parts by a crossover line, $T^*(x)$ (see, e.g., in [7]). To the right from $T^*(x)$ lies the so-called marginal Fermi liquid (MFL) regime [8] that seems to merge with the traditional FL at even larger x . Area on the left hand side is known in the literature as a “pseudogap regime” (PG). Although no consensus exists yet regarding details, the pseudogap regime seems to be spatially inhomogeneous. In particular, it was suggested (see discussion and references in [9]) that the $T^*(x)$ is the *line* for start of a 1st order transition frustrated by the electroneutrality condition in the presence of rigidly embedded dopants. If so, the area between the T -axis ($x = 0$) and $T^*(x)$ could be considered as a miscibility gap for solution of strontium holes into the La_2CuO_4 network, if it were not for the long range Coulomb forces on the part of rigid Sr^{2+} ions that prohibit the phase separation on a macroscopic scale. Therefore, at elevated temperatures this area emerges as the regime of a *dynamical* competition between two sub-phases (magnetic and metallic), as it was first suggested in [5]. Such two-component character of the PG side of the cuprates phase diagram has been firmly established at the analysis of the NMR experiments in [9]. It turned out that the ^{63}Cu nuclear relaxation rate comes about from two independent dissipative processes, related to the dynamically coexisting phases –islands of incommensurate antiferromagnetic (ICAF) phase (“stripe phase” seen in the inelastic neutron’s scattering experiments as IC-peaks near (π,π) [10]), and metallic islands (the latter probably being of a MFL character).

Numerous evidences currently fully confirm such picture for PG regime. For instance, the motion of phases may be slow down by different defects which results in the so-called “Cu wipe-out” effect observed in [11, 12, 13], provided frequencies of fluctuations get low enough to approach the NMR frequency window. Gradual “freezing” of fluctuations and subsequent glassy localization of heterogeneities has been demonstrated in [14]. Static stripes are known for the Nd- and Eu- doped LSCO [15, 16, 17]

and in LCO doped by barium, Ba, near the Ba concentration $x = 1/8$ commensurate to the periodicity of the low temperature tetragonal lattice phase [18]. Finally, the unequivocal confirmation in favor of two phase coexistence comes from the very fact that at low enough temperature (usually below T_c) the ICAF is seen in the neutron diffraction experiments [19], proving onset of their static coexistence in the real space at low temperatures [20, 21] (fraction of the ICAF phase increases with applied fields).

As it was mentioned, below we make an attempt to derive from the experimental data indications whether the amount of the Sr-doped holes determines the *total* number of charge carriers in cuprates. Our conclusion is that the number of carriers increases faster than x at higher x and T . For the electronic spectrum of cuprates, it also signifies that the Cu(d^9)-levels mix together with the holes on the oxygen ions into a common band that is studied by the ARPES experiments.

We considered the available experimental data on the Hall coefficient at elevated (up to 1000K) temperatures [22, 23, 24]. We have found that in a broad range of x and temperatures the data for carriers concentration from the Hall measurements, n_{Hall} , can be presented surprisingly well in a form

$$n_{Hall} = n_0(x) + n_1(x) \exp(-\Delta(x)/T) \quad (1)$$

(It turns out that Eq. (1) also describes new results [25]). The x -dependence of the temperature independent component, n_0 , is given in Fig.1. Aside from the scattering at small x $n_1(x)$ is practically constant (~ 2.8) up to the vicinity of $x = 0.2$, where it drops down abruptly. Note considerable deviations from the linear in x behavior in n_0 ! Although numerous factors (anisotropy, the temperature dependent scattering processes, etc.) can complicate the theoretical interpretation of the Hall effect data, it is known, however, that interactions drop out for the isotropic Fermi-liquid model [26] and even for a non-parabolic but isotropic shape of the FS [27]. Meanwhile, it is seen in Fig.1 that deviations from the linear dependence begin rather early, already at $x = 0.07$. The hole-like FS “locus” seen by ARPES, being centered at (π, π) , is practically isotropic up to $x = 0.11$ [28, 29]. Therefore even the temperature independent amount of carriers grows faster than x with doping (similar results have been reported [30] for $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_6$).

Unlike the Hall effect data for $n_0(x)$ where common interpretation becomes unreliable at larger x , the activation character of the temperature-dependent term in Eq. (1), however, is the thermodynamic feature and, as such, should not be sensitive to model scattering mechanisms. The exponential contribution describes the thermally activated carriers that come from levels lying deeply below the chemical potential.

In principle, such a term could come from different regions of the material because of its inherent non-

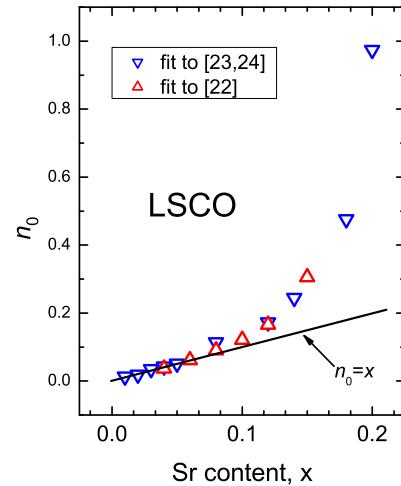


FIG. 1: The doping dependence of $n_0(x)$, obtained by the fitting of Eq.(1) to the experimental Hall coefficient temperature dependence [22, 23, 24] for LSCO.

homogeneity in the real space. We assume, however, that activated carriers are excited from some deeper parts of the LSCO energy bands. Indeed, according to the ARPES data [4, 29, 31], in addition to the “coherent” states corresponding to an “arc” on the locus of FS at the chemical potential, in the vicinity of $(0, \pi)$ and other symmetric points there are seen deeply-lying energy bands featured by the high density of electron states (so called van Hove “troughs”, or van Hove singularities). We suggest that electrons are thermally activated from the van Hove “troughs” at $(0, \pi)$ and the rest of the symmetric points, and go into the vicinity of the nodal “arc” at the chemical potential on the FS “locus” [4, 29], where the activated electrons join the liquid of mobile carriers. In order to check this suggestion we have plotted in Fig. 2 data for the energy gap $\Delta(x)$ of Eq.(1) together with the energy separating the underlying van Hove bands from the Fermi level which was deduced from Fig. 3 of [4] and Fig. 3b in [29] for various Sr concentrations (shown with red circles). For both quantities the extracted values are in an excellent agreement, thus giving the strong argument in favor of our interpretation.

A mere band singularity in density of states at the van Hove point by itself, of course, would be not enough to account for the thermodynamic activation contribution. We argue that in ARPES one measures only one component of the total energy of an electron imbedded into the lattice. In other words, implicitly, we invoke a localization of electrons near the vicinity of the van Hove points. Although from a different point of view, importance of lattice/polaronic effects at the interpretation of ARPES

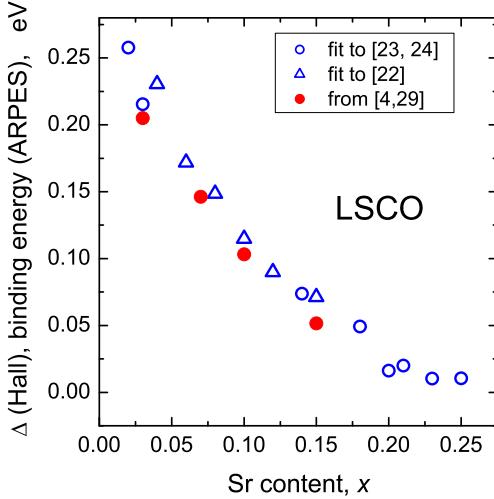


FIG. 2: The activation energy $\Delta(x)$, obtained by the fitting of Eq.1 to the experimental Hall coefficient temperature dependence [22, 23, 24] for LSCO (open circles and triangles), *vs* the energy separating the underlying van Hove bands from the Fermi level (binding energy) which was deduced from Fig. 3b of [4] and Fig. 3 in [29] for various Sr concentrations (shown with filled circles).

data has been pointed out also in [32]. (We estimate the order of magnitude for the lattice component as a few tens meV, see below).

Eq. (1) describes well the Hall data [22, 23, 25] practically in the whole available temperature interval without revealing sharp features or changes in the behavior near the line of the hypothetical 1st order transition, $T^*(x)$, mentioned above. It is worth to emphasize that there are no reasons for appearance of such features at the onset of the transition, because the transition does not realize itself: the frustrations caused by the Coulomb forces allow only fluctuations corresponding to a dynamical two-phase coexistence in the PG regime, instead of the macroscopic phase segregation. Consequently, $T^*(x)$ marks only a crossover between the left- and right hand sides of the (T, x) -phase diagram for LSCO cuprates. A good fit for $T^*(x)$ is obtained just from the comparison when the number of doped carriers, x , and activated ones become approximately equal:

$$T^*(x) \approx T_0(x) = -\Delta(x)/\ln x \quad (2)$$

In Fig. 3 we plotted $T^*(x)$ defined according to Eq.(2) and the crossover temperatures obtained differently from other experiments.

The fact that the decomposition into two contributions given by Eq.(1) covers the PG regime at smaller temperatures [23] and even reproduces well the low temperatures Hall measurements in the high fields normal state

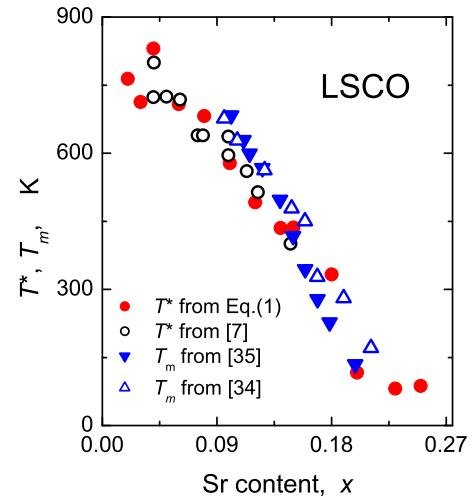


FIG. 3: The pseudogap crossover temperature $T^*(x)$ obtained: with the help of Eq.(1) with the activation energy $\Delta(x)$ shown in Fig. 2 (filled circles); from the crossover temperature of the resistivity curves (open circles); as the temperature (T_m) corresponding to the maximum of the magnetic susceptibility measured in [33] (filled triangles) and [34] (open triangles).

of LSCO [35] raises questions. In fact, to which of the two PG sub-phases one is to correlate the Hall effect data? The same question concerns the ARPES measurements.

It seems reasonable to connect the Hall coefficient, R_H , with properties of the metallic component. Indeed, if stripes were pinned by defects, and the conductivity along the stripes were expected to bear the one-dimensional character, that should suppress conduction in the transverse direction. These arguments have been tested [36] for the temperature dependence of the Hall coefficient in the Nd-doped LSCO material with different Sr content. The Hall coefficient, $R_H(T, x)$ [36] has a characteristic drop at temperatures $T \sim 70 - 100K$, at least for under-doped compositions. One finds similar features in the data [35] that even are characterized by approximately the same temperature scale. It is important that this effect is strongest for $x = 0.12$, where the fraction of the stripe phase should be maximal.

As to the second question, since the ARPES experiment is a fast measurement, it provides the instant snapshot of deep energy levels for metallic islands and probably does not change essentially when taken above or below $T^*(x)$ [37]. Making use of the excellent agreement in Fig.2 of the Hall activation energy with the ARPES results [4, 29], we have extended our gap analysis in terms of Eq.(1) to the data [23] at higher x . Notable, the result shows a plateau at x just above ~ 0.2 in Fig.2. According to [4, 28, 29], the FS “locus” experiences the topological change from the hole-like “FS” centered at (π, π) to the

electron-like one centered at $(0,0)$ very close to $x = 0.2$. “Gap” seen in Fig.2, obtained from the interpolation of Eq.(1) into this concentration range, in our opinion produces the estimate for characteristic energy scales of the lattice effects ($\sim 10\text{meV}$).

As it is known, in the ARPES experiments one start seeing the FS “locus” in LSCO already at concentration as small as $x = 0.03$. However the “FS” obtained in this way covers a large area of Brillouine zone that then changes in “agreement” with the “Luttinger count”, $1 - x$ [28]. Since currently it is established [4] that the propagating (coherent) excitations come about only in a narrow “arc” near the nodal directions, there are no contradiction between [28] and the trend seen in Fig.1 that shows that actual number of mobile carriers grows faster than x even at lower temperatures.

Since we have already touched above some issues related to resistivity of cuprates, it is worth mentioning a peculiar feature that, in a sense, is fully consistent with our general line of arguing. For extremely small Sr doping the thermal excitation of carriers gives rise to very interesting transport behavior - the temperature independent contribution to conductivity. It comes about due to the fact mentioned above that each thermally activated charge creates a local defect at the CuO_2 plane. These defects play the role of scattering centers and contribute to resistivity at high temperatures. The density of these defects equals to the density of charge carriers produced by thermal activation. Hence the same activation energy governs the lifetime of charge carriers. It results in temperature independent resistivity. This property manifests itself experimentally as saturation of the temperature dependence for resistivity at extremely low doping [24].

Contributions to the activated component of the Hall coefficient in Eq.(1) come from the vicinity of the van Hove bands that have a pronounced 1D behavior. Therefore the emptied sites should reveal a localized behavior. We suggest that activated carriers in Eq.(1) may add a temperature independent contribution into resistivity at high temperatures as well.

A simple consideration that does not compromise the ideas of the MFL [8], but may still be essential for understanding of the linear in T resistivity *well below T^** (e.g. for such doping level as $x = 0.15$ [38, 39], is that deeply inelastic scattering processes, by removing one of the conservation laws’ constraints in the ordinary FL approach, would immediately produce such linear dependence.

Finally, we note by passing the specific features in the behavior $n_0(x)$ in Fig.1 near $x \sim 0.2$ (we mentioned above the drop of $n_1(x)$ at the same x). This concentration has already been identified in a number of publications as an emerging QCP for cuprates [40, 41]. Appearance of the plateau in Fig. 3 at exactly the same concentration is in the agreement with this expectation.

To summarize, we found the quantitative agreement between the activation energies in the high temperatures

Hall data and the ARPES measurements. It also has been shown that the actual concentration of mobile carriers is not equal to the number of the externally introduced holes, even more, the carriers concentration increases with doping and temperatures. In turn, it signifies that Cu spins are not fixed at a given Cu-site. In other words, spins may move along, in agreement with other arguments [9] that consider PG region as a region of dynamically coexisting and competing sub-phases.

The authors are grateful to Y. Ando for sharing with us the recent Hall measurements data [25] prior to publication. We also appreciate helpful discussion with D. Pines. The work of L.P.G. was supported by the NFMFL through NSF cooperative agreement DMR-9527035 and the State of Florida, that of G.B.T. through the RFBR Grant N 04-02-17137.

* Electronic address: grteit@kfti.knc.ru

- [1] Emery, V. J., 1987, Phys. Rev. Lett. **58**, 2794
- [2] Varma, C. M., S. Schmitt-Rink, and E. Abrahams , Solid State Commun. **62**, 681 (1987)
- [3] Zaanen, J., G. A. Sawatzky, and J. W. Allen, Phys. Rev. Lett. **55**, 418 (1985)
- [4] T. Yoshida *et al.*, cond-mat/0510608
- [5] L.P. Gor'kov and A.V. Sokol, JETP Lett. **46**, 420 (1987)
- [6] J. Tranquada *et al.*, cond-mat/0603763
- [7] T. Timusk and B. Statt, Rep. Prog. Phys. **62**, 61 (1999)
- [8] Varma, C. M. *et al.*, Phys. Rev. Lett. **63**, 1996 (1989)
- [9] L.P. Gor'kov, G.B. Teitel'baum, JETP Letters, **80**, 221 (2004)
- [10] H. Aeppli *et al.*, Science **278**, 1432 (1997)
- [11] A. Hunt *et al.*, Phys. Rev. Lett. **82**, 4300 (1999)
- [12] N. Curro *et al.*, Phys. Rev. Lett. **85**, 642 (2000)
- [13] G. Teitel'baum *et al.*, Phys. Rev. B **63**, 020507(R) (2001)
- [14] C. Panagopoulos, V. Dobrosavljevic, Phys. Rev. B **72**, 014536 (2005)
- [15] J.M. Tranquada *et al.*, Nature **375**, 561 (1995)
- [16] J.M. Tranquada *et al.*, Phys. Rev. Lett. **78**, 338 (1997)
- [17] G. Teitel'baum *et al.*, Phys. Rev. Lett. **84**, 2949 (2000)
- [18] M. Fujita *et al.*, Phys. Rev. B **70**, 104517 (2004); M. Huecker *et al.*, cond-mat/0503417
- [19] K. Yamada *et al.*, Phys. Rev. B **57**, 6165 (1998)
- [20] A.T. Savichi *et al.*, Phys. Rev. B **66**, 014524 (2002)
- [21] B. Lake *et al.*, Nature **415**, 299 (2002)
- [22] T. Nishikawa, J. Takeda, M. Sato, J. Phys. Soc. Jpn. **63**, 1441 (1994)
- [23] Y. Ando *et al.*, Phys. Rev. Lett. **92**, 197001 (2004)
- [24] W. J. Padilla *et al.*, cond-mat/0509307
- [25] S. Ono, Seiki Komiya, Yoichi Ando (to be published)
- [26] D. Pines and P. Nozieres, The Theory of Quantum Liquids (Addison-Wesley Publishing Co., Inc., Reading, MA, 1989), Vol. 1
- [27] M. Khodas, A. M. Finkel'stein, Phys. Rev. B **68**, 155114 (2003)
- [28] A. Ino *et al.*, Phys. Rev. B **65**, 094504 (2002)
- [29] T. Yoshida *et al.*, Phys. Rev. Lett. **91**, 027001 (2003)
- [30] F. Balakirev *et al.*, Nature **424**, 912, (2003)
- [31] M. R. Norman and C. Pepin, Rep. Prog. Phys. **66** 1547

(2003)

- [32] K.M.Shen *et al.*, Phys. Rev. Lett. **93**, 267002 (2004)
- [33] R. Yoshizaki *et al.*, Physica **166C**, 417 (1990)
- [34] T. Nakano *et al.*, Phys. Rev. **B 49**, 16 000 (1994)
- [35] F. Balakirev *et al.* NFMFL, Annual Report 2005
- [36] T. Noda *et al.*, Science **286**, 265 (1999)
- [37] compare with [24]: based on the analysis of their optical data the authors [24] came to the conclusion that "the local environment of mobile holes remains unaltered by doping"
- [38] H. Takagi *et al.*, Phys. Rev. Lett. **69**, 2975 (1992).
- [39] M.Gurvich and A.T. Fiory, Phys. Rev. Lett. **59**, 1337 (1987)
- [40] C. Panagopoulos *et al.*, Phys. Rev. **B 66**, 064501 (2002)
- [41] S. Sachdev, Rev. Mod. Phys. **75**, 913 (2003)